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9. Coating of Paper and Board

Paper, composed of individual fibers, has a rough surface and pores whose size corresponds approximately to the fiber dimensions. Since this roughness has a negative effect on printing, a large amount of paper and board is coated in order to impart a smooth surface for printing. Coating is a process by which a mixture of water, white pigments, binder, and various additives are applied to one or both sides of a paper sheet. The resulting covering and smoothening of the surface of the paper improves its glaze, gloss, brightness, and above all, its printability in all conventional printing processes.

Economic Importance. In spite of the higher costs of coated papers, the proportion of the total production of paper and board that is coated has increased steadily in the last 25 years because of the quality advantages described above. Current prognoses assume that this development will continue up to the year 2000 (see Table (19)). Of the 57×10^6 t of paper produced in Europe in 1988, 12.7×10^6 t (22.3 %) were coated. However, as shown in Table (20), this percentage varies greatly from country to country depending on the structure of the paper industry in each case. The largest producer of coated paper and board in Europe is Germany, followed by Finland and Italy. About 39 % of the 5.2×10^6 t of graphic paper produced in Germany is coated, ca. 50 % of which is wood-containing, and the remainder wood-free. About 45 % (1.4×10^6 t) of the board employed for packaging (folding boxboard, liquid packaging) is coated.

Table (21) shows that between 1986 and 1988 the proportion of coated papers increased continuously both in Germany and in the United States. It should be taken into account that in the same period of time, the export of coated papers from Europe into the United States also increased and has now reached ca. $600 - 800 \times 10^3$ t. The paper manufacturers in Europe are concerned about the fact that many producers have already made or are planning considerable investments because of the favorable prognosis. The production capacity for wood-containing coated papers will increase by about 800×10^3 t and that for wood-free coated papers by 2.4×10^6 t from 1990 to 1992. It is questionable whether this drastically increased supply will meet with an equally high demand. The enormous capital required for these new investments—a new paper machine and coating machine cost about 500×10^6 DM—has previously led to the closing down of companies, even in Europe.

Coated Paper and Board Grades. The classification of coated grades has not yet been standardized. However, certain terms are recognized throughout Europe.

Art Paper. This term refers to wood-free or slightly wood-containing paper that is coated on both sides. The weight of the coating exceeds 20 g/m^2 per side, resulting in the complete disappearance of the fiber structure of the raw paper. These papers can be either dull or glossy. Up to three coats are applied to each side to obtain the high quality required. Art paper is used for high quality printed products.

Chromopapers. Chromopaper is coated only on one side. However, the weight and quality of the coating correspond to that of art paper. Much of this paper is employed for packaging purposes.

Machine-Coated Papers. This term was previously used only for papers coated on-machine. Today, it is also applied to papers which are coated off-machine and have a similar coating weight and appropriate quality. It includes both wood-free and wood-containing papers with a

coat weight of up to 18 g/m² per side. Higher weights are often obtained by applying a double coat. The coating formulations are normally simpler than those for art paper. The covering of the fiber structure depends on the particular coating weight and the roughness of the base paper. Machine-coated papers are used chiefly for printing.

Lightweight Coated (LWC) Papers. The English term is used internationally for this grade of paper. These papers are highly wood-containing and generally have coat weights in the range 5–12 g/m² per side. They are mass papers and are used for the production of catalogs, magazines, advertising pamphlets etc. The fiber structure can still be discerned in most cases. Either web offset or rotogravure printing is used for LWC paper. The total weight of LWC papers varies between 51 and about 71 g/m². From about 1982 the weight range has been extended below (ULWC or LLWC) and increasingly also above (MWC=medium-weight coated and HWC=high-weight coated) these limits. Today, the heavy grades are often provided with a double coat and are, consequently, grouped with machine-coated grades.

Cast coated papers are specialty paper and board grades. The mirror-like gloss is obtained by a process called cast coating, in which the still moist or remoistened coating surface is brought in contact with a highly polished cylinder and dried. Only one side is coated in most cases.

Folding Boxboard and Chromoboard. In these grades of board, the white topline, which is usually made of pulp, is coated on the board machine. The remaining layers of board can consist of bleached or unbleached pulp or of wastepaper. However, the use of wastepaper for the topline is also rapidly gaining acceptance. The coating weight is in the range 12–25 g/m² and the coat is normally comprised of a precoat and a topcoat. Recently, three coating layers have also been applied. The board is rarely coated on the reverse and if it is, it is mainly to improve the flatness and to reduce dust deposition. High-gloss board is produced by using a brush finishing system or a gloss calender.

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9.1. Requirements of Coated Papers

The composition of the coating color is largely determined by the demands made on the surface of the paper by the particular printing process. Offset and letterpress printing require an especially well bound coat because considerable tensile forces are exerted by the highly viscous inks at the high printing speeds used today. At the same time, the coating must be sufficiently porous to permit fast, controlled removal of the printing ink vehicle without reducing the gloss of the ink. For offset printing, the surface of the coating must have not only an especially high water resistance, but also the ability to absorb sufficiently quickly the fountain solution applied in the printing machine. In general, coatings must have adequate stiffness, good brightness, low yellowing tendency, and good aging resistance.

In rotogravure printing, the tensile forces between the printing cylinder and the surface of the paper are very small because of the low viscosity, solvent-containing inks that are used. For this reason, the amount of binder required should only be sufficient to bind the pigment particles to each other and the paper surface so that picking of the coating is prevented during the further processing of the coated rotogravure paper. Important criteria for coated papers that are to be used for rotogravure printing are good compressibility, a high degree of smoothness, and adequate receptivity for the ink solvent.

Apart from the optical and printing properties, there are other criteria that are important for paper and board used for packing purposes. These include low odor, flexibility, glueability, and crease resistance. Coated specialty papers require specific properties, such as alkali resistance (labels), washability (wallpaper), and solvent resistance (silicone release paper).

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9.2. Properties and Components of Coating Colors

Apart from water, the main components of a coating color are coating pigments and binders. In addition, a variety of auxiliary agents, such as dispersing agents for the pigments, additives to reduce wet abrasion, products for the control of viscosity and water retention, foam control agents, shading dyes, optical brighteners, and lubricants to improve paper calendering, are employed. Coating colors, which are almost without exception all water-based, are fairly complicated multicomponent systems. Nowadays, paper is coated on high speed coating machines that are either a part of the paper machine or separate from it (on- or off-machine coaters). Coating colors are classified according to their solids content:

- 1) Low-concentration coating colors, solids content 35–45 %; Newtonian flow behavior; viscosity (Brookfield method) 100–500 m Pa·s (at 100 rpm, 20 °C); coating process or equipment: a) air knife, b) bar coater (for low coating weights)

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Satin white is still of some importance in paper coating. This pigment has very fine particles; it is extra white, and has a low density. It increases ink absorption and gloss. The disadvantages of satin white are its sensitivity to increases in temperature and decreases in pH, and its high adhesive demand.

In spite of the high price and limited availability of titanium dioxide, it is employed especially in the United States to compensate for the yellowish U.S. clay. As a result of its high refractive index, this pigment greatly increases the opacity of coated paper, even in the wet state. For this reason, it is used in Europe mainly for specialty papers (e.g., labels).

9.2.2. Dispersing Agents

The first stage in the production of coating colors is the conversion of the coating pigments, which are usually supplied in the dry state, into a flowable and pumpable aqueous slurry. This dispersion process consists of two steps: the mechanical dispersion of the coarse pigment agglomerates in an aqueous medium and the chemical stabilization of the slurry towards reagglomeration. The second step requires dispersing agents.

Suitable dispersing agents are polyanions, e.g., salts of polyphosphoric acids (pyrophosphates, hexametaphosphates) or poly(acrylic acids). These products permit the production of stable, highly concentrated pigment slurries that are still flowable. Coating colors with concentrations of 70 % and more can be produced. Today, ready-for-use pigment slurries are often available from pigment suppliers. The specific requirement of dispersing agents for the individual pigments varies greatly. English clays, for instance, require ca. 0.3 % and American clays ca. 0.1 % of dispersing agents. Calcium carbonates need 0.4–0.8 %, depending on the fineness and the pretreatment, and satin white requires 2–3 %. The protective colloid action of organic dispersing agents stabilizes the rheological properties of the coating color, especially in the case of satin white.

9.2.3. Binders

The function of the binder or adhesive is to bind the pigment particles to each other and to fix the coat to the base paper. In spite of their low proportion by weight in the coating color (generally 5–25 % based on the pigment), binders have a large influence on the coating and processing properties of the coating color.

Binders from Natural Raw Materials. The natural binders all have hydrophilic properties. The most widely employed binders of this type are starch and its derivatives, cellulose ethers such as carboxymethyl cellulose, and in the United States, hydroxyethyl cellulose, soybean protein, and to a very small extent casein and alginates.

Natural binders act as protective colloids that prevent the flocculation of the pigments; they increase the viscosity and water retention of coating colors and give the coat a higher stiffness. In general, natural binders are used as additives for synthetic polymer binders.

Starch derivatives are intended to lend the coating color good rheological properties at high shearing forces. They should have a good pigment-binding power and ensure good adhesion of the coating to the paper. In order to meet these and other requirements, mixtures with other binders, and variation in type of derivatives are used. For example, oxidized starches are usually employed

together with polymer dispersions. Hydrolyzed starches exhibit high stability in solution, good binding power, and good flow behavior. Hydrolyzed, esterified starches exhibit good stability in solution, high binding power, and increased reactivity towards wet-strength additives such as urea-formaldehyde resins. Hydrolyzed, etherified starches exhibit the same properties as the esterified derivatives. However, in contrast to the esterified derivatives, they can be used at pH values above 8 without the risk of saponification. Starch derivatives that contain phosphate and amino groups are compatible with cationogenic substances such as satin white. The phosphate groups react with multivalent metal ions, such as aluminum ions, which in turn leads to a certain degree of water resistance. The amino groups react with aldehydes, which in turn enhances the activity of wet-strength additives.

Cellulose Ethers. The sodium salt of carboxymethyl cellulose (CMC) is the principal cellulose ether used as a binder in papermaking. Pure CMC coats of 0.5–3 g/m² increase the grease resistance and printability of paper. Depending on the use, various mixtures of low- and high-viscosity CMC are employed. Pigment-containing CMC coats, which can be applied on the size press, contain up to 10% semitechnical, low-viscosity CMC or salt-free, purified CMC. CMC is usually processed together with other natural or synthetic binders. Above all, CMC increases the water retention of the coating mixture. However, the water retention is so high that the addition of other binders that promote water retention in the coat to a lesser extent is necessary. In general, the amounts of CMC employed are 0.3–1.5% based on the pigment, and very low viscosity types are preferred. This gives an adequate coating color viscosity, even if the solids content of the coating color is high. Types of CMC that are soluble in cold water are rapidly becoming established because they do not require dissolving at elevated temperature. The presence of satin white pigment can cause strongly interfering coagulations in the coating color.

Casein must be present in the dissolved state. It is dissolved by the addition of alkali (e.g., ammonia, sodium hydroxide, borax, or sodium carbonate) either separately in a cooker (up to 70 °C) or with the pigment in a kneader. The casein concentration is limited to ca. 20% by its high viscosity. The limit of processability is shifted to ca. 33% by the addition of urea or dicyanodiamide, which reduces the viscosity and increases the storage stability of casein solutions. The mixing of casein solutions with pigments, especially China Clay, can cause a "shock" phenomenon (a rapid increase of viscosity).

Soybean protein has properties very similar to those of casein. Isolated soybean proteins are hydrolyzed, isoelectric proteins. They are used in the form of alpha and delta proteins with four different viscosities (extra low, low, medium, and high). The viscosity refers to the dissolved soybean protein, the solvent of choice being aqueous ammonia (26 Bé). Proteins dissolved in this way exhibit very low sensitivity to water after drying. Like casein, soybean protein is mostly used as a mixture with polymer dispersions. This combination permits the preparation of coating colors with high solids content and a relatively low viscosity. Solids contents of ca. 60%, suitable for blade coaters, can be achieved.

Synthetic Binders. In the initial phases of paper coating, natural binders were used exclusively. However, in the 1940s in the United States and in 1950s in Germany, the demand for synthetic binders in the form of polymer dispersions started increasing. These products made it possible for the first time to attain a high solids content at low viscosities, a prerequisite for modern high-speed coating machines. In addition, polymer dispersions give the coat a higher water resistance, better flexibility, higher gloss, and better printability. The products employed today are aqueous dispersions of polymers, usually stabilized with anionic emulsifiers. The solids content of the dispersions is generally 45–50%. In most cases, the polymers are copolymers of several monomers, e.g., styrene, butadiene, acrylic ester, vinyl acetate, and acrylonitrile. Apart from these components—the so-called main monomers—small amounts of auxiliary monomers, such as

acrylamide, acrylic acid, maleic acid, and methacrylamine are added to modify the dispersion properties.

The styrene-butadiene dispersions are most widely used worldwide. Products of varying film hardness are obtained, depending on the proportion of styrene used. The compatibility of these highly hydrophobic polymers with the other coating components can be improved considerably by carboxylation, i.e., by incorporating small amounts of unsaturated carboxylic acids such as acrylic acid. Approximately equal proportions of styrene and butadiene give binders which provide a relatively soft film and a very good pigment binding capacity. However, the odor of the dispersion and the tendency of the films to yellow when exposed to light are disadvantages.

Acrylate dispersions are of comparable importance in Europe. These are copolymers of butyl acrylate with styrene or vinyl acetate. The ratio of the soft component (butyl acrylate) to the hard one (styrene or vinyl acetate) determines the application characteristics of the dispersion. In general, acrylate dispersions have an excellent ageing resistance and are less odorous. Apart from these two most important groups of polymer dispersions, vinyl acetate homo- or copolymers have gained entry into paper coating plants, especially in the United States. These products generally have a lower binding power, but provide very hard and porous coats, and have an excellent ageing resistance. Polymer dispersions based on methacrylates and copolymers of vinyl acetate and ethylene are less important in paper coating.

The above-mentioned products are low-viscosity aqueous dispersions which usually do not influence properties such as viscosity and water retention that are important for the flow behavior of the coating. For this reason, only in a few cases are these "multipurpose dispersions" used alone. They are usually mixed with cobinders, which are responsible for adjusting the flow properties of the coating color. In general, these cobinders are naturally occurring products, such as starch, casein, CMC, and alginate.

Recently, products based on acrylate esters have also been used as cobinders. Due to their high degree of carboxylation, these dispersions turn into colloidal dispersions upon addition of alkali. Thus the laborious and energy consuming dissolving and cooking processes involved in the use of natural binders are avoided. Another synthetic cobinder that has long been known is polyvinyl alcohol. Although its binding power exceeds that of all other binders used in paper coating, it has gained only limited acceptance. This is mainly due to the fact that the application of large amounts of polyvinyl alcohol leads to rheological problems on the coating machine during processing.

Apart from these two-component systems, synthetic sole binders which do not require a cobinder have been available since the early 1960s. On addition of alkali, these products develop the required viscosity and water retention, but retain their dispersion form. Special binders of this type have become popular, especially for illustration paper that is produced in large amounts and printed by the rotogravure or web offset process. Table (22) lists the various binder systems, their influence on the production of coating colors, the rheological properties of the coating color, and the coating properties.

9.2.4. Other Additives

In many coated papers and boards, the coating must be resistant to water. For instance, offset papers are exposed to the fountain solution in the printing machine, labels should not disintegrate when wet, and some wallpapers must be resistant to cleaning with detergents.

Good waterproofing of coatings can be achieved by using water-insoluble polymer dispersions. However, additional auxiliary agents are required to harden the coating since a water-soluble cobinder is used in most cases, which renders the coat sensitive to water to some extent. Three Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition on CD-ROM. ©1997 WILEY-VCH, D-69451 Weinheim, Germany.

main classes of products are employed as hardening agents: melamine-formaldehyde resins, urea-formaldehyde resins and bifunctional aldehydes such as glyoxal, which is added only to coatings containing starch. The other two resins are used in various binder combinations. High proportions of natural binders require the addition of 10–15 % of hardening agents, based on the natural binder. For sole-binder coatings or coatings with only very small amounts of cobinder, 0.8–1 % is used, based on the pigment.

The waterproofing of the coating is due to a cross-linking reaction between the resin and the binder, with elimination of water. The rate and degree of cross-linking depend on the pH and the temperature. The desired effect increases with decreasing pH of the coating color and intensity of drying. The worldwide discussion on formaldehyde being a possible carcinogen has led to an intensified search for other cross-linking systems. For instance, products based on ammonium zirconium carbonate or epoxides are being used in some cases.

Foam-control agents (→ Foams and Foam Control) are another important class of additives. Most coating colors contain considerable amounts of products that act as foam producers or stabilizers (e.g., emulsifiers, protective colloids). Due to the constant motion of the coating color, air is easily introduced into it. The resulting foam causes an increase in viscosity and processing problems. However, the more serious problems are flaws in the finished coat such as craters and longitudinal streaks caused by the bursting of foam bubbles. The foaming tendency decreases with increasing solids content and is, therefore of minor importance for modern high-solids coatings. The use of appropriate systems that minimize the ingress of air during preparation and circulation of coating color is the principal measure taken to prevent foam. However, in many cases this is not sufficient and chemical defoamers must be added.

A distinction is made between agents that prevent foam formation (foam inhibitors) and those that destroy foams (defoaming agents). Coating color defoamers must not only be easily emulsifiable, but should also be worked into the coating color under an appropriately high shear gradient. Otherwise, or if too much is used, agglomerates of defoamers are formed in the coating and these in turn lead to spots of low surface energy where printing ink will not adhere (fish eyes). In practice, the amounts of foam inhibitors used vary from 0.02 to 0.05 %, based on the pigment. Defoamers are usually diluted with water and added to the coating mixture dropwise. Amounts ranging from 0.01 to 0.05 vol % are usually sufficient.

In many cases, the yellowish color of the coating clay does not satisfy market requirements. Apart from the addition of pigments such as titanium dioxide which increase brightness, blue-violet dyes (*shading dyes*) are often used at a concentration of about 2 g per 100 kg of pigment to attain a bluish white coating surface which appears brighter to the eye. Not only basic dyes, but also the considerably more lightfast pigments may be used. If the brightness required is very high, *optical brighteners* are added in addition (→ Optical Brighteners). In order to be effective, most optical brighteners need a substance to which they can be attached. Substances of this type are polyvinyl alcohol, carboxymethyl cellulose, casein, starch, and some synthetic cobinders. Polymer dispersions do not have this property.

So-called *lubricants* such as calcium or ammonium stearate are used in many illustration papers to reduce dusting on the calender and produce a higher paper gloss.

9.2.5. Coating Color Formulations

The coating color formulations presented below are examples of formulations commonly used in Europe at present. However, they must usually be adapted to suit the particular conditions in the

Starch is used only rarely in the topcoat. CMC or a synthetic acrylate based cobinder is preferred for board.

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9.3. Coating Color Preparation

A flow sheet for the batch production of coating colors is shown in Figure (83). These, or similar plants that permit adaptation to a very variable coating program, are used in practice in by far the most cases.

Water, dispersing agent and, when required, alkali are fed to the dispersing machine and the dry pigments are then added. While kneaders were used previously for dispersion, high-speed mixers with rotor-stator systems have now gained acceptance. These turbomixers permit the production of a completely dispersed pigment slurry in 5-60 min, depending on the amount of pigment. The next step is either the intermediate storage of the slurry or the immediate preparation of the coating color in the turbomixer, depending on the size of the plant. Dispersion requires the highest rate of rotation, but the speed is reduced when binding and auxiliary agents are added. Natural binders such as protein or starch are dissolved in advance by heating in a separate vessel.

When adding the binding and auxiliary agents, the amount of water required to give the desired final solids content is added to the pigment slurry first. The natural cobinders are then added with constant stirring, followed by the polymer dispersion, and finally the auxiliary agents, such as hardeners, shading dyes, optical brighteners, and lubricants. This is followed by the final adjustment of the pH, viscosity, and solids content, and pumping the mixture into the storage vessel.

The pigment slurry and also the finished coating color are screened at least once before they enter the coating machine. The use of a screen in the coating color return flow is also recommended to remove particles torn off the paper. Pressure or disk filters or vibrating screens are used for the filtration of the coating color. The mesh size of the screens is 5000-10 000 apertures/cm². Coarser screens with mesh sizes of 2500-3500 apertures/cm² are required for clay. Apart from batch plants, continuous plants also exist and they have the advantage of requiring less space, and the amount and composition of coating color can be more easily changed. The precondition for a continuous plant is that all the components of the coating color are present in the liquid state. They are then transferred to the dispersion apparatus by dosing pumps. After passing through the shearing zone the finished coating color leaves the closed system.

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